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High pressure study of the intramolecular vibrational modes in sexithiophene single crystals

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Abstract

We report on the effects of a high hydrostatic pressure on the intra-molecular modes of a sexithiophene (T6) single crystal. Raman experiments were performed at low temperature up to a pressure of 80 kbar. We find that intermolecular interaction gives rise to a sizeable redistribution of the intensities of the strongest intra-molecular Raman lines. These changes are due to a slight deformation occurring in the terminal rings of the sexithiophene molecule. The frequencies of the bending modes involving sulfur atoms are the most affected by pressure. A Davydov doublet and a mixed inter/intra-molecular mode are observed. These results confirm the role played by the sulfur atoms in modulating the electronic overlap between chains.

Keywords: Raman spectroscopy; Organic semiconductor based on conjugated molecules; High pressure; Intermolecular interaction

1. Introduction

Sexithiophene (T6) has attracted strong interest in the last years for its electronic and optical properties such as the high carrier mobility [1,2] and the sizeable stimulated emission [3]. This molecule is one of the model compounds [4,5] most widely used to understand the basic aspects of electronic structures and optical properties of conjugated polymers.

Inter-chain coupling of molecular materials can dramatically alter the electronic and optical properties in the bulk as compared to isolated chains [6,7], e.g. in polythiophene interchain screening has been suggested to reduce the binding energy of the 1 Bu exciton from 1.85 eV for decoupled chains to 0.76 eV for the bulk material [8]. The most definitive way to study *how* and *why* this phenomena occur is to monitor the influence of the variation of intermolecular distance achieved by applying hydrostatic pressure [9]. This method avoids the use of chemical modifications which usually affect not only the intermolecular interaction but also the conjugated backbone. Moreover, pressure permits to obtain a comparatively small variation of the interchain interaction.

Hydrostatic pressure acts on molecular solids in a two-step process. Pressure acts directly on the intermolecular distances but it leads to important intramolecular phenomena too, like changes of molecular conformations (symmetry) and variation of force constants (bond strength). Vibrational spectroscopy is a valuable tool to study the conformational and electronic properties under pressure, through the observed changes of energies, intensity and widths of vibronic transitions as a function of intermolecular distance. In fact, a change of symmetry can lead to the variation of the selection rules and, therefore, the (dis)appearance of vibrational modes while the variation of the force constants can lead to a shift in the mode frequencies.

In this viewpoint, Raman scattering is an efficient and relatively easy technique to probe disorder, structural changes, phase transitions and inter-chain interactions in molecular materials at high pressure [10,11]. We have performed to our knowledge the first 10 K Raman investigation on T6 single crystals from ambient up to 80 kbar.

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2. Experimental

The T6 single crystals were grown by sublimation under argon atmosphere [12]. Pressure studies were conducted in a Merrill–Bassett-type diamond anvil cell (DAC) with cryogenically loaded argon as the pressure medium and ruby luminescence was used as pressure calibrant. No broadening of the ruby luminescence was detected up to 60 kbar, and only a slight broadening above 60 kbar, indicating that the applied pressure was hydrostatic. Raman measurements were carried out in a back-scattering configuration, using the 488.0 nm line of an Ar-ion laser. The Raman spectra at 0 kbar was measured using the 647.1 nm line of a Kr-ion laser, due to the strong photoluminescence background observed exciting with the 488.0 nm line. The laser photon energy 2.541 eV is close to the strong electronic transition at 2.597 eV towards the upper Davydov level b_u. The scattered light was detected with a SPEX triple monochromator equipped with a charge-coupled device (CCD) detector and a holographic supernotch filter. To perform the low temperature measurements, the DAC was attached to the cold finger of a closed-cycle cryostat. A Lorentzian curve fitting routine was used to determine the frequencies and intensities of Raman modes.

3. Results and discussion

The lattice of T6 single crystal is monoclinic with four molecules in the unit cell. The molecules in the crystal have a herring-bone arrangement with two molecular layers in the unit cell. The interaction between two molecules in adjacent layers is head to tail, giving rise to an interlayer electronic coupling much weaker than the intra-molecular one. The T6 single crystal belongs to the space group $P2_1/n$, with a factor group isomorphic to the C_{2h} point group. The T6 molecules in the crystal show an elevated planarity [12,13] due to the large packing effect [14], with deformation and torsional angle of the thiophene rings around 1° [12].

The resonant Raman spectra of conjugated molecules shows few lines that are selectively enhanced originating from totally symmetric modes [15]. The strong enhancement of these modes is associated with their strong electron–phonon coupling to the dipole allowed electronic transition [16–20]. The Raman spectra, measured in resonant condition under pressure are shown in the two spectral windows presented in Figs. 1 and 2. The region around 1333 cm^{-1} is not shown, since it is dominated by the strong Raman mode of the diamond. The region between 300 and 750 cm^{-1} is associated with the bending of the sulfur atom (CSC). The most intense of these bands is at 697 cm^{-1} (Fig. 1). In the region below 900 cm^{-1}, our spectra show some broad features which have been attributed [18] to the out of plane movements of the carbons next to the sulfur. The modes between 1000 and 1400 cm^{-1} mostly involve stretching of the carbon (CC) and bending of the hydrogen (CCH) [18]. The lines between 1400 and 1600 cm^{-1} (Fig. 2) are attributed

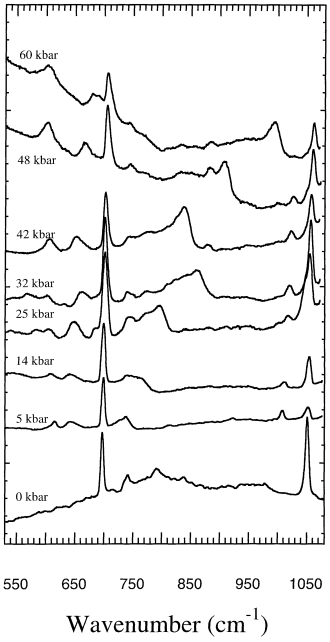

Fig. 1. Raman spectra of T6 single crystal at different pressures ($T = 10$ K). The absolute intensity of the spectra can not be compared. The 32 kbar spectra has been taken after a rapid decrease of pressure from 80 kbar. All spectra except the 0 kbar excited with the 647.1 nm line of a Kr-ion laser were excited with the 488.0 nm of an Ar-ion laser.

to the stretching of the carbons bonds (CC) [18]. In this region, the most intense Raman mode (1459 cm^{-1}) is observed. The strongest Raman lines show only a slight broadening (<3 cm^{-1}).

The evolution of the Raman spectra with increasing pressure (up to 60 kbar) is shown in Figs. 1 and 2. The

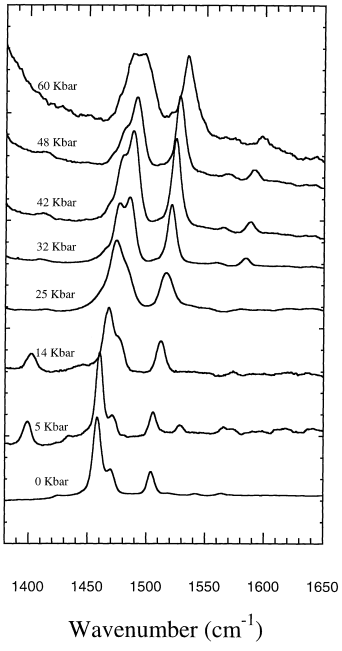

Fig. 2. Raman spectra of T6 single crystal at different pressures ($T = 10$ K). All other parameters as in Fig. 1.

frequency and intensity of the strongest intra-molecular modes at 699, 1051, 1460–1470 and 1504 cm^{-1} exhibit a good reversibility with pressure cycles.

Other new bands emerge in the Raman spectra when the sample is under hydrostatic pressure. New modes appear at 616, 642, 765 (at 14 kbar), 1008, and 1399 cm^{-1}. These bands are not present at ambient pressure, and only the mode at 616 cm^{-1} has been previously reported [18] while the mode at 642 cm^{-1} has been observed under resonant conditions as a weak feature for T6 powders [21].

The pressure dependence of the frequency of the Raman active modes is reported in Fig. 3. Aside from the modes around 600 cm^{-1}, the frequency of the vibrational modes strongly increases with pressure. This behavior is caused by the stiffening of the bonds. A convenient way to describe this effect on a given mode frequency v_i is to consider the mode Grüneisen parameter γ_i that can be expressed as [11]

$$\gamma_i = -\left(\frac{V}{v_i}\right)\frac{\mathrm{d}v_i}{\mathrm{d}V} = \frac{1}{\kappa}\frac{\mathrm{d}(\ln v_i)}{\mathrm{d}P} = \frac{1}{v_i\kappa}\frac{\mathrm{d}(v_i)}{\mathrm{d}P} \quad (1)$$

where V is the volume of the crystal, κ the compressibility, and P the pressure.

For three-dimensional covalent inorganic semiconductors in which only one kind of bond is involved in the crystalline network, all γ_i's are the same. When weak intermolecular (Van der Waals) bonds are present together with strong intramolecular covalent bonds [10], as in molecular solids, the γ_i's are not frequency independent. γ_i's span a range of several orders of magnitude, and follows an approximate scaling law $\gamma_i = v_i^{-2}$ in going from inter-molecular (higher γ_i) to intra-molecular modes (lower γ_i) [11,22]. The variation of γ_i reflects the expected higher shrinking with pressure of the intermolecular distances with respect to the intramolecular ones [23,24].

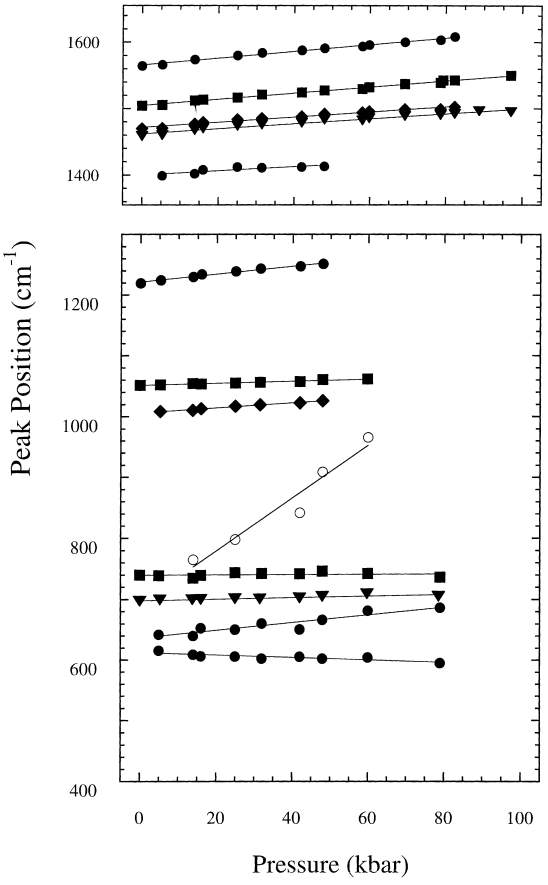

Fig. 3. Pressure dependence of the Raman modes.

Table 1 reports the frequencies of the measured Raman modes (at the lowest pressure), their assignments, and $(1/v_i)\,\mathrm{d}v_i/\mathrm{d}P$ which are proportional to the Grüneisen parameters. The very large value γ_i for the new band at 765 cm^{-1} reflects the extremely large shift (roughly 200 cm^{-1} between 14 and 60 kbar) with pressure. A similar huge frequency

Table 1
Raman frequencies at ambient pressure and respective $(1/v_i)\,\mathrm{d}v_i/\mathrm{d}P$[a]

Raman modes (cm^{-1})	Assignments	$(1/v_i)\,\mathrm{d}v_i/\mathrm{d}P$ ($kbar^{-1}$)
616*	Bending CSC (o, m)	-3.2×10^{-4}
642*		9.8×10^{-4}
697	Bending CSC (i, m)	1.8×10^{-4}
765*		4.3×10^{-3}
1008*		4.1×10^{-4}
1051	Stretching CβCβ (i) and Bending CCH (I)	1.6×10^{-4}
1219	Bending CCH (I) and Stretching CαCβ (o)	5.4×10^{-4}
1399*		2.2×10^{-4}
1459	Stretching CβCβ (i, m)	2.6×10^{-4}
1470	Stretching CαCα (m) and Stretching CβCβ (m)	2.6×10^{-4}
1504	Stretching CαCβ# (o)	3.0×10^{-4}
1565	Stretching CαCβ (i)	3.2×10^{-4}

[a] The modes are assigned as in Ref. [18]. We denote the modes by identifying the atoms which experience the strongest displacement for the different modes. αα refers to modes between carbon atoms of neighboring rings, ββ is related to carbons not linked to the sulfur in the thiophene ring and αβ refers to modes between the carbon that is in the α position and the C-neighbor in the same thiophene ring. The letters i, m, and o (inner, middle and outer) indicate the position of the ring local oscillator on the molecule. The frequencies marked by * are revealed only under pressure (5 or 14 kbar). The modes marked by # involve mainly the two carbon atoms at the end of the T6 molecule.

shift was reported only for intermolecular modes [10,22,23]. We believe that only overtones involving inter-molecular modes or vibration with mixed intra/inter-molecular origin can explain such a behavior [22–24]. As the frequency of the external phonons is expected to be in the range of a few tens of cm^{-1} [22], the mixed vibration should implicate vibrations around 750 cm^{-1}. Modes in this frequency range involve the sulfur atoms which should, therefore, play an essential role in modulating the electronic overlapping between molecules. Similar conclusions were drawn concerning the influence of sulfur atoms on the carrier transport in T6 films [25,26]. Except for the doublet 616–642 cm^{-1}, the behavior of which will be discussed in the next paragraph, the Grüneisen parameters of the other modes are much smaller as expected for intramolecular phonons. For these vibrations, γ_i's do not decrease monotonously with mode frequency but show a rather irregular behavior. This behavior can be understood only if we consider that the large number of atoms in the T6 molecule gives rise to complex intramolecular vibrations. In the following, we discuss in detail the behavior as a function of pressure of the strongest Raman modes. Namely, the CSC bending modes at 600–700 cm^{-1}, the new intra/inter-molecular mode, the CH bending mode at 1050 cm^{-1}, and the CC stretching modes at 1450–1500 cm^{-1} which present sizeable frequency variations and intensity changes.

A negative γ_i for a given phonon mode (soft mode) — as that observed for the CSC mode at 616 cm^{-1} — is often taken as the signature of the crystal lattice instability against the atom displacement induced by the soft mode. In the T6 crystal we show the softening to be due to the interlayer coupling between CSC bending vibrations.

To do so, the behavior of both the 616 and 642 cm^{-1} lines with pressure is reported in Fig. 4. The two lines move away with pressure [27] as expected for a Davydov doublet [28] when the mode interaction increases. This doublet originates from the splitting of the vibrations corresponding to the translational non-equivalent molecules, induced by their mutual interaction in the crystal [29,30]. The splitting gives rise to four internal modes (A_g, B_g, A_u, B_u), two of which are Raman-allowed (A_g, B_g). The frequency of the un-split mode at ambient pressure is estimated by extrapolating the bisecting line of the linear curves of the doublet to 0 bar which yields 624 cm^{-1}. This estimate is in very good agreement with the value obtained by means of ab initio calculations (626 cm^{-1}) considering a unit cell with four non-interacting T6 molecules [18]. The 626 cm^{-1} mode is attributed to an in-plane bending of the sulfur atom mostly *localized* at the outer thiophene rings (Table 1) [18]. For this reason, it is mainly affected by the interlayer interaction.

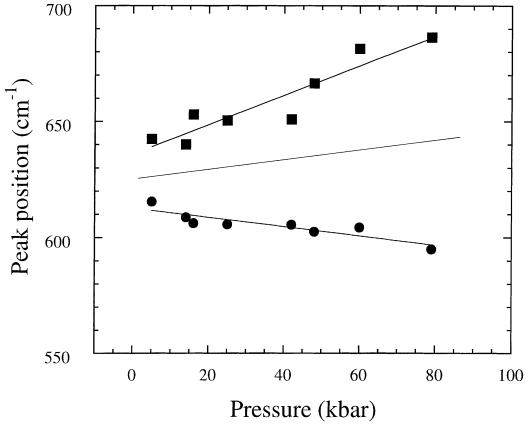

Fig. 4. Behavior of the 616, and 642 cm^{-1} modes with the pressure. The linear regression curves for the two modes are shown together with the extrapolation of the un-split mode. The frequency of the un-split mode is estimated by means of the bisecting line of the linear regression of the doublet.

This analysis is further supported by the negligible influence of pressure on the mode at 696 cm^{-1}. This vibration originates from the same kind of vibration but mostly involves the *inner* rings of the T6 molecules and thus weakly affected by interlayer interaction. The lack of any Davydov splitting of this inner mode indicates that the in plane CSC vibrations of a T6 molecule of the crystal is very weakly coupled with the same vibration in neighboring molecules of the same layer. This conclusion could appear in contrast with the fact that intralayer electronic coupling is certainly stronger than interlayer interaction. The frequency stability of the CSC inner bending mode on pressure can be only understood if we consider that the atomic displacements for this normal mode are along the molecular axis. These intramolecular atomic motions imply a negligible modulation of the intermolecular distance *within* a layer, yielding a negligible *intralayer* mode coupling. It is interesting to note also that the 1051 cm^{-1} mode does not show any Davydov splitting. As the CSC bending mode at 696 cm^{-1}, this vibration is related to a CH in-plane bending vibration localized at the inner part of the T6 molecule.

Raman spectra of oligomers of different lengths [17,20] show that the CSC bending mode is quite sensitive to chain length, displaying a softening of the CSC bending mode on going towards shorter chains down to T2 where its frequency is 676 cm^{-1}. In polythiophene, the dispersion of this mode with chain length has been used to identify the reduction of the effective conjugation length induced by distortion of the backbone [17]. The small linewidth and frequency variation of the inner bending vibration demonstrates that the effective conjugation length of the T6 chain is negligibly influenced by pressure.

As far as the line broadening is concerned, it is quite important to note that the Davydov doublet shows a considerably larger line width which can be the signature of a certain amount of disorder in the layer stacking. A higher broadening is also observed for the vibration with mixed intra and inter-molecular character at 750–800 cm^{-1}. Disorder in the local packing of the molecules is the result of the weak intermolecular interaction. The possibility of different metastable intermolecular configurations is clearly shown in the Raman spectrum at 32 kbar which has been taken just after a rapid decrease of pressure from 80 kbar. In this

spectrum, the Davydov splitting of the bending mode at the outer rings and the frequency of the vibration with mixed character are both larger than the corresponding values at 42 kbar. Conversely, the intensity and frequency of the most intense Raman lines which have genuine intra-molecular character, do not present this singular behavior.

Finally, we note that, upon increasing pressure, the relative intensity of the outer mode of the CSC bending (see Fig. 1) vibration increases with respect to the inner modes. A similar behavior has been found for the two Raman bands at 1459–1470 and 1504 cm^{-1} which also corresponds to CC stretching modes of inner and outer rings (Fig. 2) (see Table 1), respectively.

In order to discuss this behavior, we recall that the Raman intensity of a mode i is proportional to the square of the resonant Raman tensor, proportional to the quantity [16]

$$\sum_{v} \frac{\mu_{ge}\mu_{eg}\langle 0|v\rangle\langle v|i\rangle}{\hbar(\omega_{ev,g0} - \omega_1)i\Gamma_{ev}} \tag{2}$$

In this equation, $\omega_{ev,g0} - \omega_1$ is the detuning between the laser frequency ω_l and the frequency of the vibronic transition $\omega_{ev,g0}$ from the ground vibrational and electronic state g to the vibrational modes v of the excited state e; μ_{ge} the transition moment; and $\langle 0|v\rangle\langle v|i\rangle$ the Frank–Condon integrals. This expression can be rewritten as a quantity proportinal to the product of a purely resonance factor $(\mu_{ge}\,\mu_{eg})/(\omega_{eg} - \omega_l + i\Gamma_e)$, and a factor Δ_i^e, which is the projection of geometrical relaxation that occurs in the excited state along the normal coordinate i. In the present experiments, the laser photon energy 2.541 eV is close to the strong electronic transition at 2.597 eV towards the upper Davydov level. Changes in the resonant factor in Eq. (2) should have a similar effect on all the strongest Raman lines. Anyway, absorption measurements show that the frequency of the upper Davydov level [31] is hardly affected by pressure while absorption at ω_l weakly increases. Therefore, the relative variation of the Raman intensities has to be related to a variation of the vibronic coupling Δ_i^e. It is also worth pointing out that the relative intensities of these lines are weakly dependent on the polarization of the incoming and outgoing photons [18], ruling out, in this way, depolarization effects induced by the diamond anvil cell. The relative enhancement of the outer modes can be caused by a slight static geometrical relaxation of the end rings — similar to the dynamic distortion due to the associated vibrations — which mostly support the interchain stress. Distortion should mostly occur in the plane of the molecules, since the enhanced vibrations involve in-plane atomic motion and also because out-of-plane geometrical relaxations are strongly inhibited by intralayer interaction.

4. Conclusions

We have presented a Raman investigation of the intramolecular modes in a T6 single crystal under hydrostatic pressure. Pressure induces noticeable changes in the Raman spectrum. The most relevant experimental findings are:

1. Inter-molecular interaction gives rise to a sizeable redistribution of the intensities of the strongest intramolecular Raman lines. These changes are discussed in terms of a slight deformation occurring in the terminal rings of the T6 molecule.
2. The frequencies of the bending mode involving sulfur atoms are the most affected by pressure. A Davydov doublet and a mixed inter/intra-molecular mode are observed. These results confirm the role played by the sulfur atoms in modulating the electronic overlapping between chains.

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